FOSSIL ENERGY

ADSORPTION CALORIMETRY OF WATER-WET
AND OIL-WET MINERALS

Topical Report

By
Leo A. Noll

March 1986

Work Performed Under Contract No. FC22-83FE60149

National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

**National Energy Technology Laboratory
National Petroleum Technology Office
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by

Dr. Leo A. Noll[1]

ABSTRACT

This project is a continuation of a research program designed to understand and model adsorption of enhanced oil recovery (EOR) chemical flooding material onto reservoir minerals. The understanding and modeling of adsorption will ultimately lead to an effective way to select EOR chemicals which are most cost effective. This report describes progress made from Oct. 1, 1984 to Sept. 30, 1985. It is divided into three parts: (1) modeling of adsorption, (2) adsorption of surfactants from solutions of brine and aqueous cosurfactant, and (3) proving the usefulness of titration calorimetry. In the first part, the surface described was water-wet; in the other parts, surfaces of different wettability were used in the investigations.

The adsorption of cosurfactant from hydrocarbon onto silica is modeled by a Langmuir isotherm. This model indicates that the adsorption is driven by enthalpy, taking place with an unfavorable entropy change. It is physical adsorption and does not exceed monolayer coverage.

Strong brine seems to have little effect on the adsorption of nonionic surfactant, except in the case of Florisil, a magnesia containing silica. For this mineral, adsorption is more energetic from brine than from fresh water. In the presence of cosurfactant, the energy of adsorption is in general higher than that from pure water. All of these enthalpies of adsorption are negative, thus implying lower adsorption as temperature is raised.

The titration calorimeter has proved to be a useful instrument for studying adsorption. This report shows that the presence of a non-reacting solid in the reaction vessel does not disturb the measurement of enthalpies of reaction. The measurement of the interaction of nonionic surfactant with silica show satisfactory agreement with the results of the flow calorimeter. Adsorption on kaolin, bentonite, and sandstone can be measured with this instrument, whereas these solids are not amenable to flow calorimetry.

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INTRODUCTION

Chemical loss by adsorption, phase trapping, and precipitation is a serious problem in the implementation of enhanced oil recovery (EOR) by surfactant-polymer flooding. Even if chemicals are not lost, chromatographic separation of an EOR slug leads to poor performance. To improve the predictability of the chemical flooding process, experiments to aid in the basic understanding of adsorption have been performed at the National Institute for Petroleum and Energy Research. This report will cover three areas: modeling of alcohol loss from hydrocarbon on a water-wet surface, silica; preliminary experiments in the use of titration calorimetry to study solid-surfactant interactions; and adsorption of surfactant from aqueous brine and aqueous cosurfactant solutions.

EXPERIMENTAL

The experiments described in this report were performed in one of two calorimeters. The "flow" experiments were performed in an LKB 2107 adsorption calorimeter in which a bed of solid is placed in the calorimeter and solvent or solution pumped through this bed. Figure 1 shows the block diagram for this instrument. Fluid comes from one of a group of source bottles, the desired liquid being selected by the Altex six-way valve. A peristaltic pump forces the fluid through heat exchangers for temperature equilibration; it then flows through the solid sample in the calorimeter cell and passes out of the calorimeter through the differential refractometer and on to "waste."

The other instrument used was a Tronac 458 titration calorimeter. This instrument consists of a stirred dewar reaction vessel into which titrant is driven by a motorized syringe. In this instrument solid and liquid can be made into a slurry, and the chemical of interest, e.g., surfactant, can be titrated into this slurry. The temperature change is sensed by a thermistor. This titration method is convenient when the solid is a clay or a powdered sandstone which would not be amenable to the flow system.

All adsorption experiments were conducted at 25° C.

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RESULTS

Modeling of Cosurfactant Adsorption

Modeling the adsorption process has been of importance to understanding the mechanisms of adsorption loss (chemical requirements) of enhanced oil recovery chemicals. For this modeling process, we have chosen a cosurfactant (1-decanol), a hydrocarbon (n-heptane), and a silica surface. The silica gel has a BET area of 340 m^2/g, and was activated by heating overnight at 300° C. Flow adsorption calorimetry of this system was carried out using 13 solutions of increasing concentration of alcohol up to a mole fraction of 0.025.

The thermal data are shown in figure 2; this is the average of four separate runs. The surface excess data are similar, but have less curvature. To model these data, a Langmuir isotherm is used. This isotherm is described by

$$\frac{X_2}{\Delta_{1,2}H} = \frac{1}{kH_m} + \frac{X_2}{H_m} \qquad (1)$$

where X_2 is the mole fraction of alcohol in the decanol-heptane solution, $\Delta_{1,2}H$ is the enthalpy of replacement of hydrocarbon by alcohol on the silica, k is an interaction parameter similar to an equilibrium constant, and H_m is the enthalpy for complete replacement of hydrocarbon by alcohol. An analogous relationship can be written for the amount adsorbed in which the parameters n_m and b replace H_m and k, respectively. Figure 3 shows the data fit to this equation. This figure shows that the fit to a straight line is good; therefore, the fit of equation 1 is good. Table 1 gives the fitting parameters for this model. In this table, the surface excess data ("amount adsorbed") are fit to equation 1. These data and fitting parameters indicate that the adsorption process is physical in nature, the enthalpy per mole being of the same order of magnitude as a hydrogen bond in water. The area per molecule does not indicate multilayer adsorption.

The surface excess is a close approximation for the amount adsorbed, provided that X_2 is less than 0.1. Using this approximation, the equilibrium constant (k) for the process is 2326 (see table 1).

From the standard relation

$$\Delta G^o = -RT \ln k \qquad (2)$$

we can obtain the free energy of this process which is -19.3 kJ/mol. From the relationship

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (3)$$

the entropy of the process can be determined as -120 J/(mol deg). This unfavorable entropy contribution indicates that there is considerable ordering of the solute molecules upon adsorption as compared with their state in the solution.

In an earlier study of the adsorption of 1-dodecanol from toluene, the enthalpy per mole of alcohol, H_m/n_m, was -33.2 kJ/mol, and k was about 115. These differences occur because of the stronger interaction of toluene with the surface than that of n-heptane. The suggestion is that losses of polar EOR chemicals from an aromatic petroleum might be less than that from an aliphatic one.

Adsorption of Surfactant From Brine and Aqueous Cosurfactant

The minerals used in this study were selected to model very water-wet and very oil-wet conditions. They are Davison silica gel, grade 62 (SiO_2) alumina (Al_2O_3), Florisil (a magnesia-silica), and reverse phase silica gel (C_{18}-SiO_2). The reverse phase silica gel was made from the above silica gel by grafting octadecyl groups onto as many polar sites as possible and then end-capping with methyl groups. The SiO_2, the Al_2O_3, and the Florisil are water-wet surfaces, while the C_{18}-D62 is an oil-wet surface. The specific areas of these minerals are listed in table 2. There is almost no interaction of Triton X-100 (TR) with alumina in fresh water, so Al_2O_3 was not used with TR in brine. Similarly, there is little interaction of SiO_2 with sodium dodecyl sulfonate (SDDS) in fresh water, so SiO_2 was not used with SDDS in aqueous cosurfactant.

At the start of each run, the enthalpy of immersion of the mineral into solvent was measured. Table 2 shows the results of this immersion step, and

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also lists the results of immersion of the minerals in distilled ("fresh") water. These results, as well as the replacement results reported below, are the average of at least two experiments.

Table 2 shows that the enthalpy of immersion for these three surfaces is slightly lower for immersion into brine and aqueous cosurfactant as compared with that into fresh water. The oil-wet surface shows the greatest percentage difference of the four surfaces.

After the immersion was completed, surfactant solution was passed through the bed of mineral. The thermal effect ("enthalpy of replacement" or "heat of adsorption") was measured as well as the extent of reaction (properly called "surface excess amount," usually referred to as "amount of adsorbed"). The results are shown in table 3.

From the data shown in table 3, some interesting calculations can be made. Two of these calculations are the molecular parking area (area available for each molecule on the surface) and the enthalpy of adsorption in units of joules per mole of surfactant. The results of these calculations are shown in table 4.

An examination of these tables suggests that the adsorption of the nonionic surfactant Triton X-100 is not greatly influenced by the presence of brine as opposed to fresh water. The greatest influence of the brine is with the Florisil. This influence is shown in both the enthalpy of immersion and in the amount adsorbed from the brine solution. The presence of magnesium in the Florisil seems to make a larger difference in the behavior of the material as compared with pure silica gel. For the silica and the oil-wet surface, the amount adsorbed slightly increases in this fairly strong brine.

The results with the aqueous cosurfactant are quite different. For each of the surfaces and for both surfactants, the energy of interaction increases as the surfactant concentration increases from 1 percent to 4 percent. The exception again is in the case of Florisil adsorbing Triton which is constant.

In most cases the molecular parking area is larger for surfactant adsorbed from either brine or aqueous cosurfactant than from fresh water. When the molecular parking area increases, the adsorption density decreases. As an approximate comparison, an SDDS molecule requires about 0.53 nm^2 when packing with the head down and the tail up. The areas shown in table 4

indicate that the surfactant molecules may be partially "lying down" on the surface. The strength of the interaction suggests that the interaction is physical. Since the enthalpies are all negative, the extent of adsorption should decrease with increasing temperature.

Titration Calorimeter: Feasibility Studies

The use of the titration calorimeter was described above. Several chemical calibrations were performed to ensure that the Tronac calorimeter was performing correctly. In a representative calibration, 24.86 ml of 0.00402 M tris-(hydroxymethyl)-aminomethane was titrated with 0.100 M HCl. Each titration increment corresponded to 9.2 sec, and during the period of active heat generation this corresponded to the addition of 0.0613 ml titrant to the reaction vessel.

To show that the presence of solid in the titration system did not invalidate its measurements, several chemical calibrations were carried out with silica gel in the reaction vessel. The calculated heat release from experiments with and without solid in the reaction vessel showed an enthalpy of reaction of -47.3 J/mol compared with the accepted value of -47.5. The results are within the precision of our HCl solution preparation. Figure 4 shows this comparison. Two separate runs are shown on this figure. These data show both the reproducibility of this experimental method as well as the fact that a non-interacting solid does not disturb the titration process.

Previous work has shown that Triton X-100 (TR) adsorbs on silica gel. Before studies were made of this interaction, it was necessary to perform dilution experiments to serve as a background or "blank" for the titration of the solid. Figure 5 shows the results of diluting 10 percent, 20 percent, and 30 percent (by mass) solutions of TR. The final concentration in the calorimeter is about one-tenth of the initial concentration.

Table 5 also gives the results of these and the other dilution experiments. This table indicates the amount of heat produced by diluting approximately 2.4 mL of stock surfactant tenfold. The negative signs indicate an exothermal result.

Figure 6 shows the results of the titration of silica gel with 30 percent TR. This figure shows the dilution of surfactant on the same axes as the

titration of the silica. The difference between the curves indicates an easily measurable interaction of the TR with silica. To a first approximation the measure of the interaction is the difference between the curves. However, each point on the curve for dilution of surfactant shows the thermal data for dilution from stock solution to a particular final concentration. When an adsorbing solid is present in the reaction vessel, the final concentration is lower than is the case for the corresponding point on the dilution curve. Samples of the solution in the reaction vessel at the end of each run have been taken. These final concentration data will be used in making the proper corrections. Computer code is being developed for this purpose.

In figure 6 the right-hand side of the curve for silica is approaching the same slope as the dilution curve, suggesting that the surface is approaching saturation with surfactant. The first approximation shows about 1.59 J difference between the curves, which corresponds to 3.04 J/g. In the flow calorimeter, -3.36 J/g was found for the enthalpy of replacement of water by TR. Even with this approximate figure, the agreement is good and indicates that the titration method can be related to our previous experiments.

Figure 7 shows the results of using a hydrophobic solid in the titration calorimeter with 30 percent TR. The solid is octadecylsilanized silica gel (C18-D62). This material is so hydrophobic that it tends to float. Figure 7 suggests that there is a cooperative interaction shown by the S-shape curve. The energy of interaction is almost twice as large on a per gram basis as that for the silica. The reason for this larger interaction is that water does not interact well with C_{18}-D62; thus, the surfactant need not compete with the water.

Figure 8 shows the titration of wood charcoal with 30 percent TR. The charcoal's capacity for TR is not yet saturated, and its energy of interaction is quite high.

Figure 9 shows the result of dilution of 5 percent TRS 10-410 and the titration of 4.34 grams of powdered Berea sandstone. The dilution of TRS 10-410 is endothermal. This petroleum sulfonate was used as received and not deoiled. Solutions of concentration higher than 5 percent tend to separate into two layers, so they were not used as titrants. Except for a few points at the beginning, the curves run parallel to each other. These few points represent the interaction which is very small (the ordinate on the graph

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represents 0.1 cal).

In addition to these experiments in which pure water was the solvent, some preliminary investigations of the effect of added salt were also performed. TRS 10-410 was prepared in 7,500 ppm NaCl brine. This solution is quite turbid. A small amount of darker, viscous material slowly settles to the bottom of the bottle. The data for figure 10 were gathered before the presence of this layer was found. The solution was thoroughly agitated and then loaded into the syringe of the calorimeter. The solution was diluted into a sample of the same 7,500 ppm brine used to "dissolve" it. The resulting dilution curve differs greatly from the TRS 10-410 made up in and diluted with fresh water. The added salt may have suppressed the CMC to a low enough level that the dilution is merely diluting the micelles. The effect may be the result of the very high ionic strength. The exact nature of the difference would require further study of this system. For the present, the dilution curve is needed if it becomes necessary to study adsorption from this turbid solution.

In addition to these representative figures, a few other entries in table 6 are of interest. The titration calorimeter has been used with kaolin and bentonite clay. The difference in behavior of these two clays is striking: the interaction on bentonite is almost three orders of magnitude larger than that of the kaolin. These clays cannot be studied with aqueous solutions in the flow system since it is not possible for aqueous solutions to flow through them. The studies with Berea also show promise, as it is difficult to prevent fines from escaping from the flow cell; however, they cannot escape from the reaction vessel of the titration calorimeter.

CONCLUSION

Progress has been made in developing a better understanding of the adsorption process by modeling. The differences occurring when adsorbing from brine or aqueous cosurfactant have been demonstrated using surfaces of different wettability. The titration calorimeter shows great promise for studying adsorption on reservoir rock samples as well as on clay for the selection of cost-effective chemicals for enhanced oil recovery.

Future efforts will be to create an adsorption data base and fit the data to models. Algorithms for the calculation of results from the titration

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calorimeter will be developed. Studies of adsorption of newer surfactants such as ethoxylated sulfonates on minerals will be undertaken.
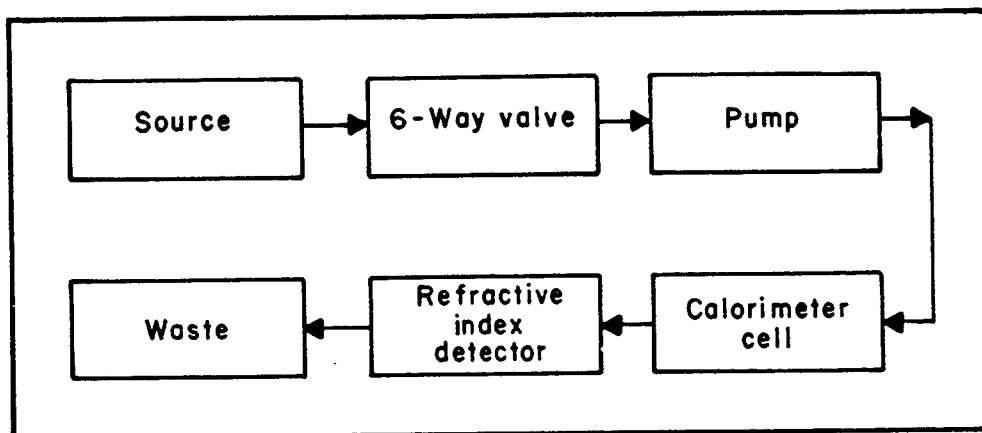
FIGURE 1. - Block design of LKB flow system.

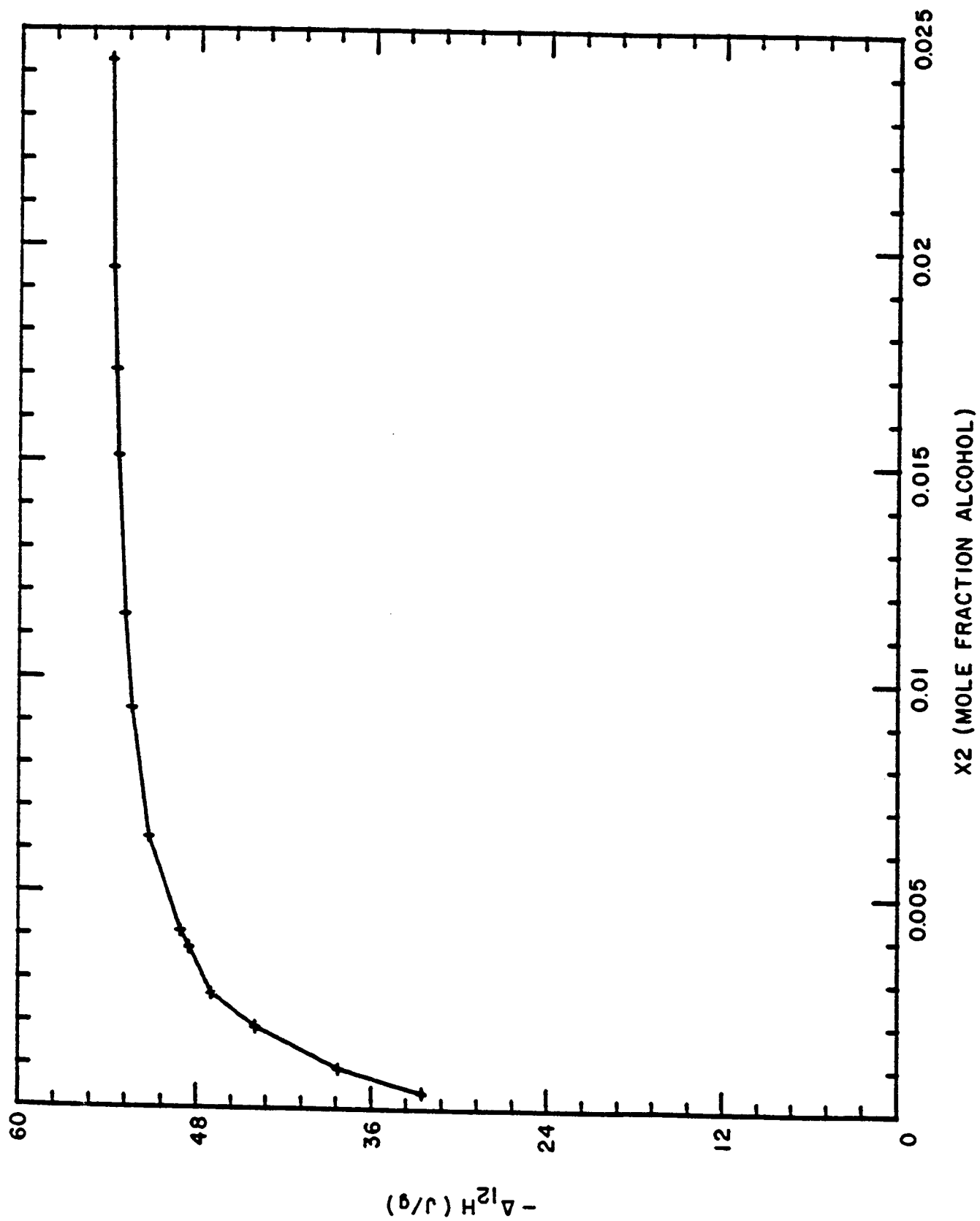FIGURE 2. - Thermal data from adsorption of 1-decanol from n-heptane on silica.

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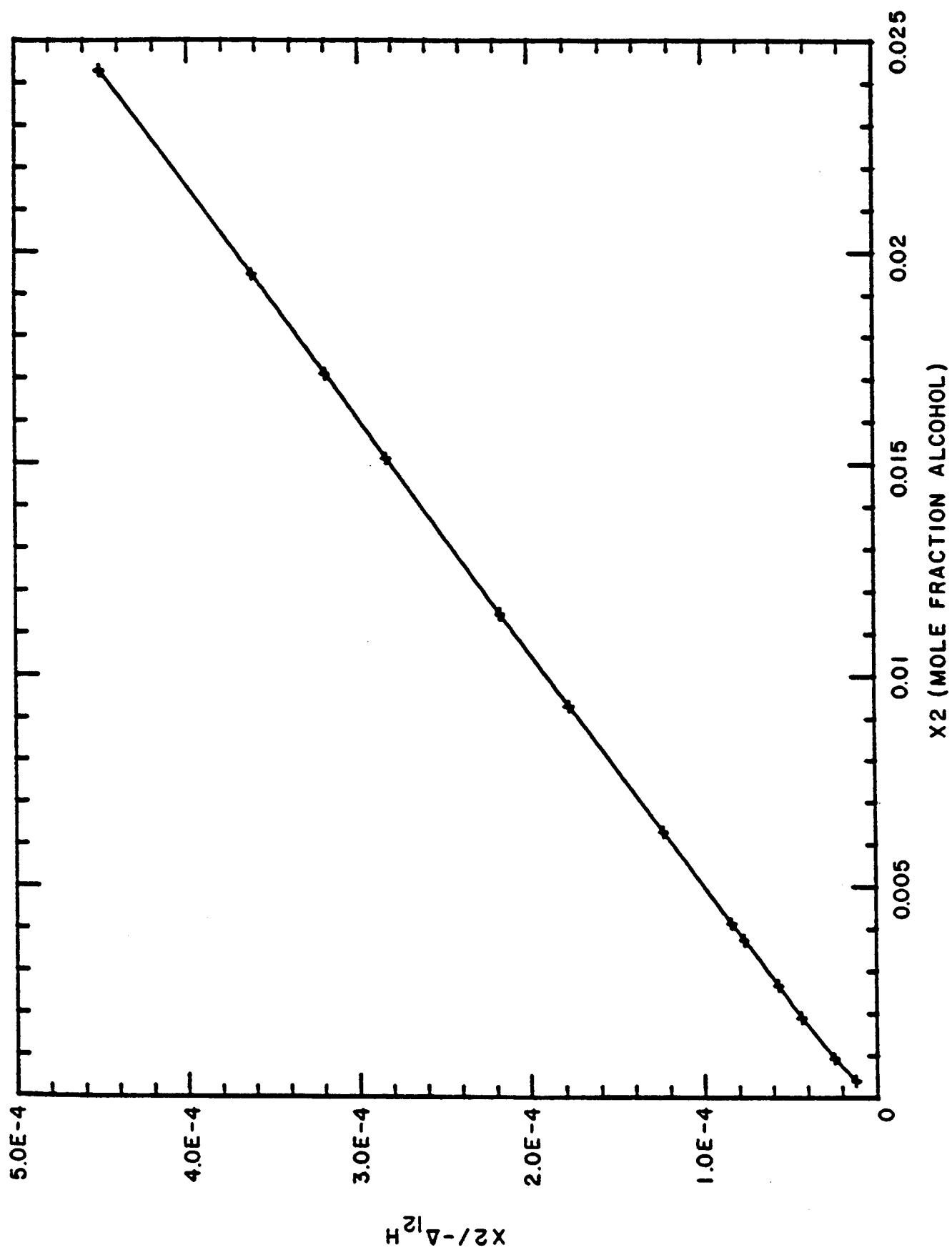
FIGURE 3. - Langmuir fit of thermal data.

X2 (MOLE FRACTION ALCOHOL)

$X2/-\Delta_{12}H$
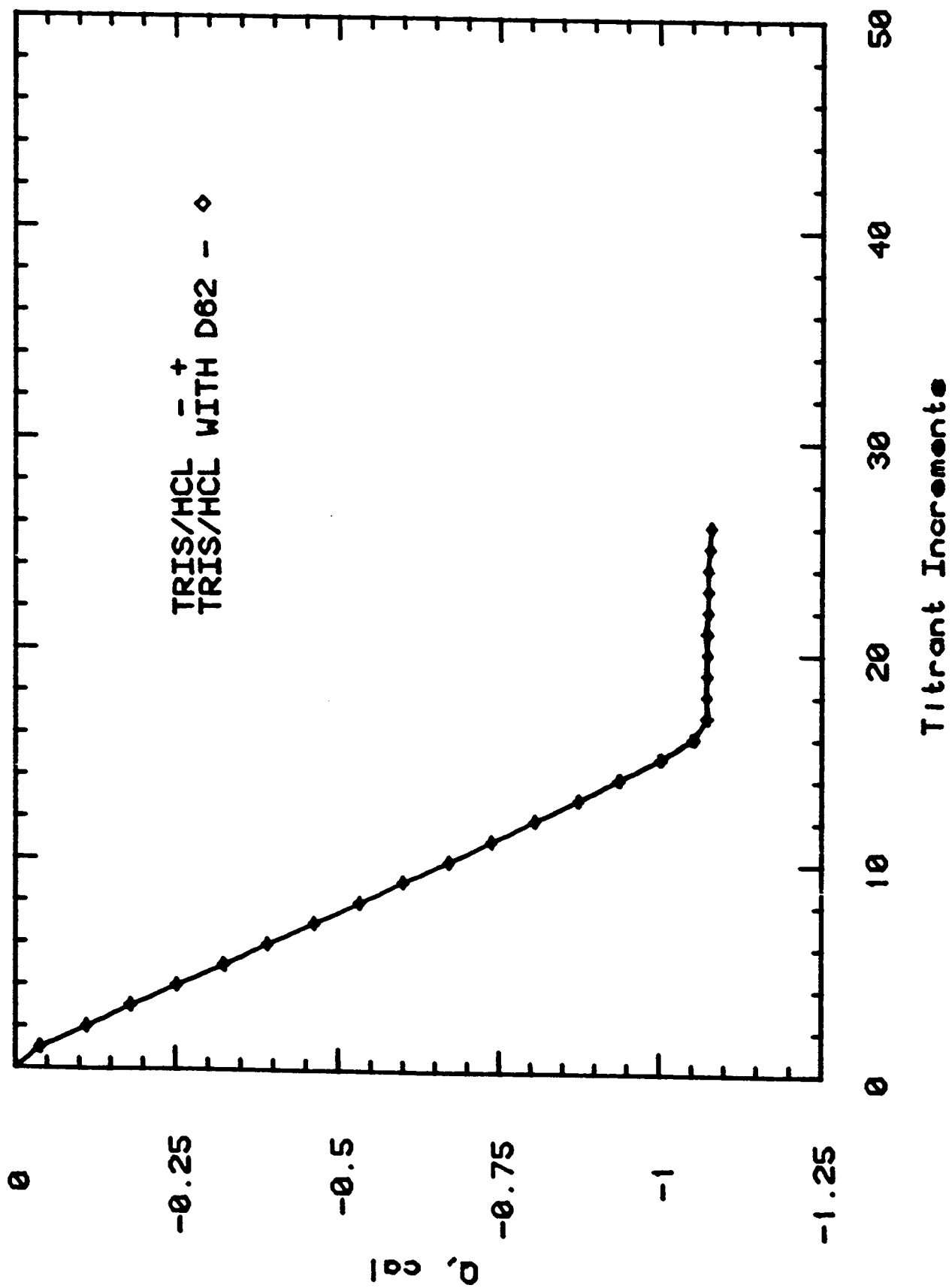
FIGURE 4. - Comparison of TRIS 1 HCl with and without silica gel in the reaction vessel.
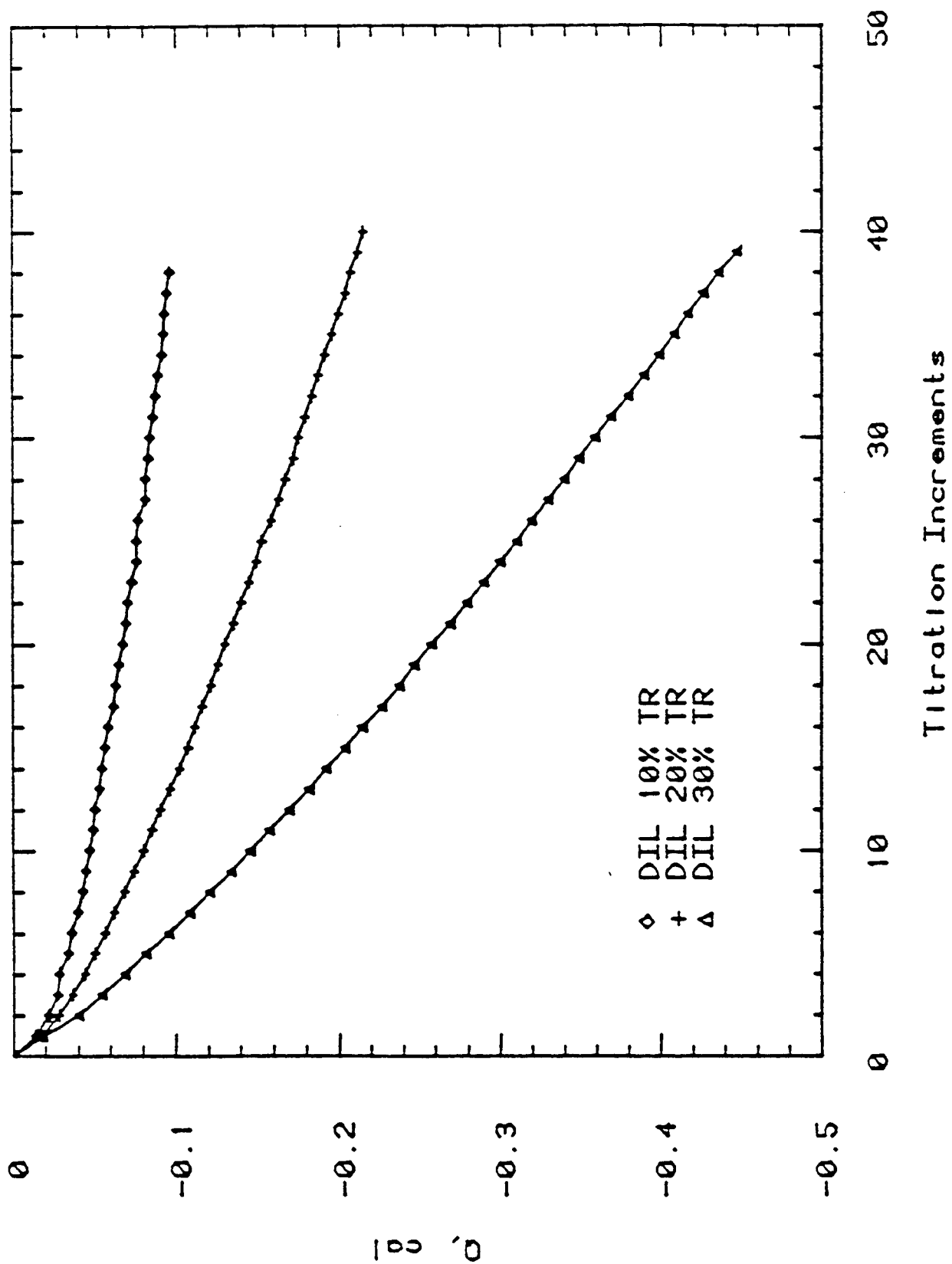
FIGURE 5. - Dilution data for 10%, 20%, and 30% Triton X-100.
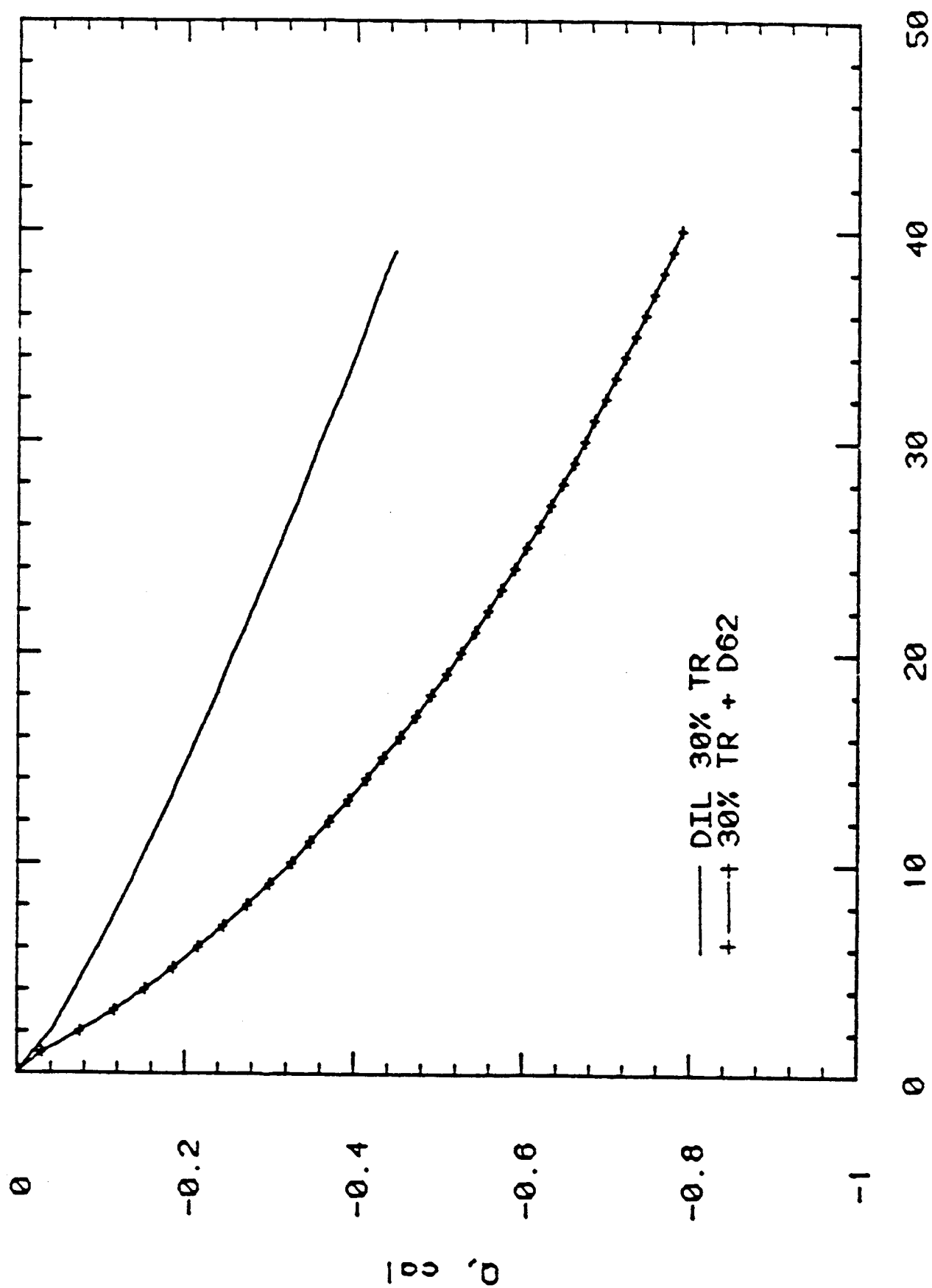
FIGURE 6. - Titration of silica by 30% Triton compared with dilution of the surfactant.

DIL 30% TR
+ 30% TR + D62

Q, cal

Titrant Increments
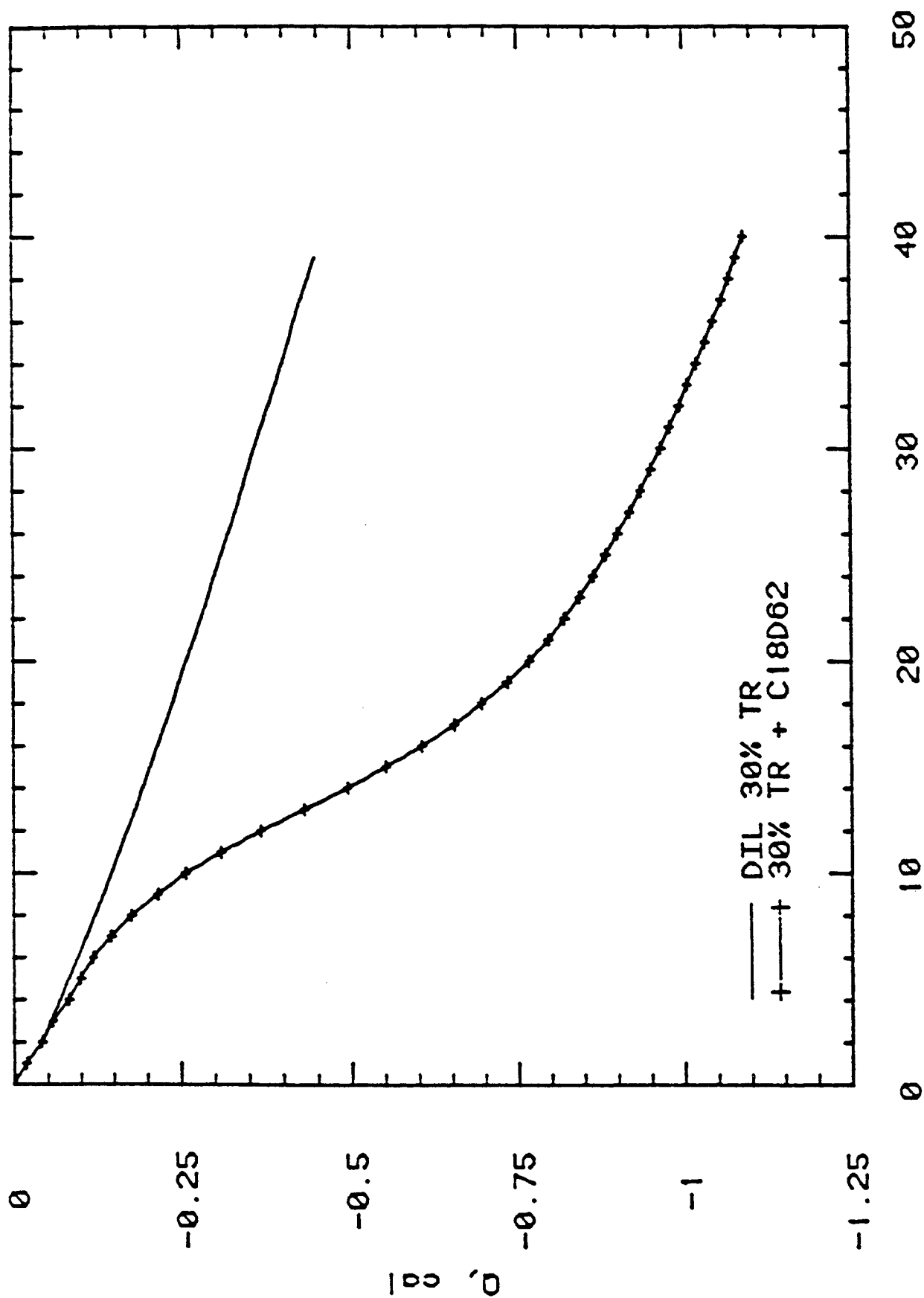
FIGURE 7. – Titration of octadecylsilanized silica by 30% Triton compared with dilution of the surfactant.

Axis label (x-axis): Titrant Increments

Axis label (y-axis): Q, cal

Legend:
DIL 30% TR
+ 30% TR + C18D62
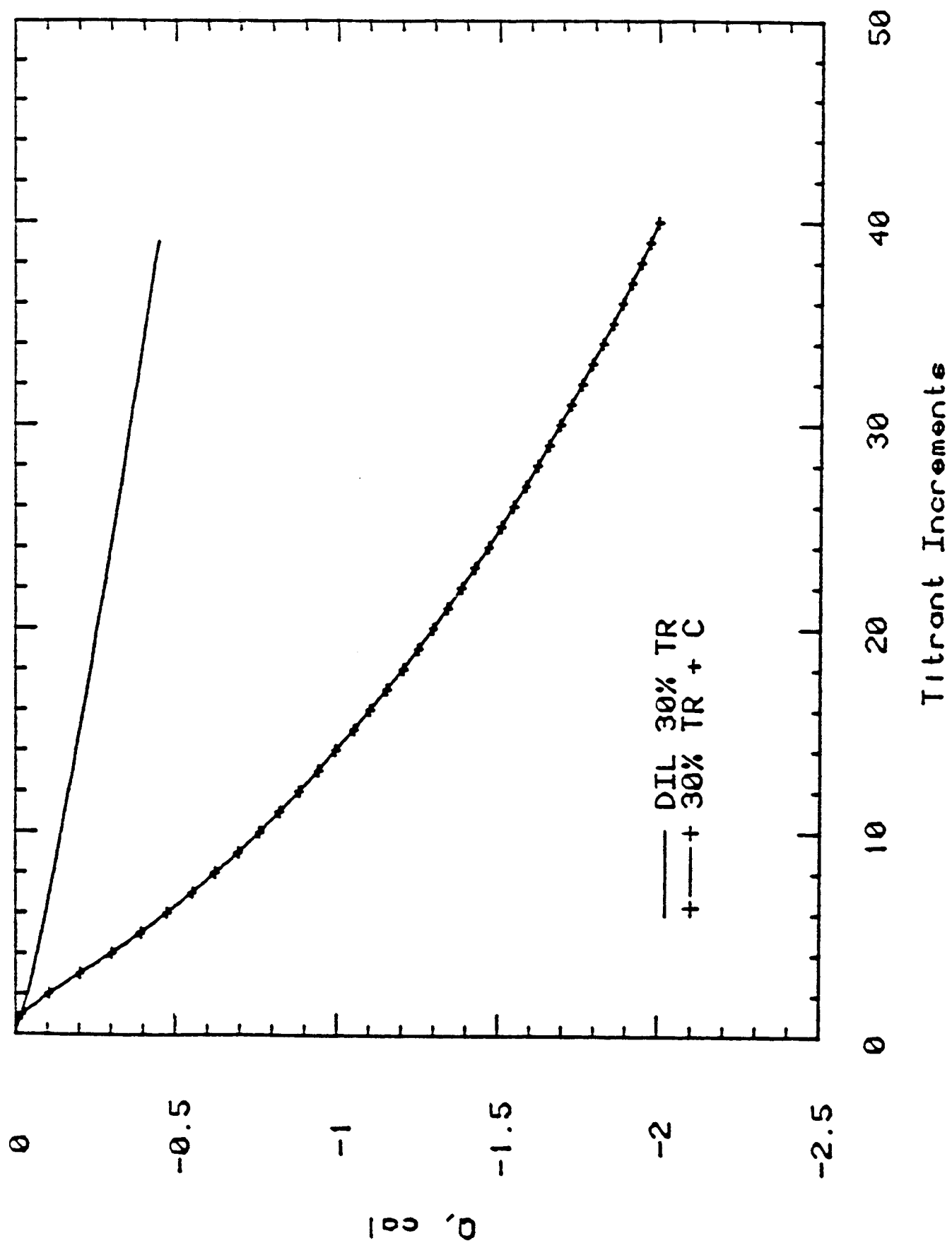
FIGURE 8. - Titration of charcoal with 30% Triton compared with dilution of the surfactant.
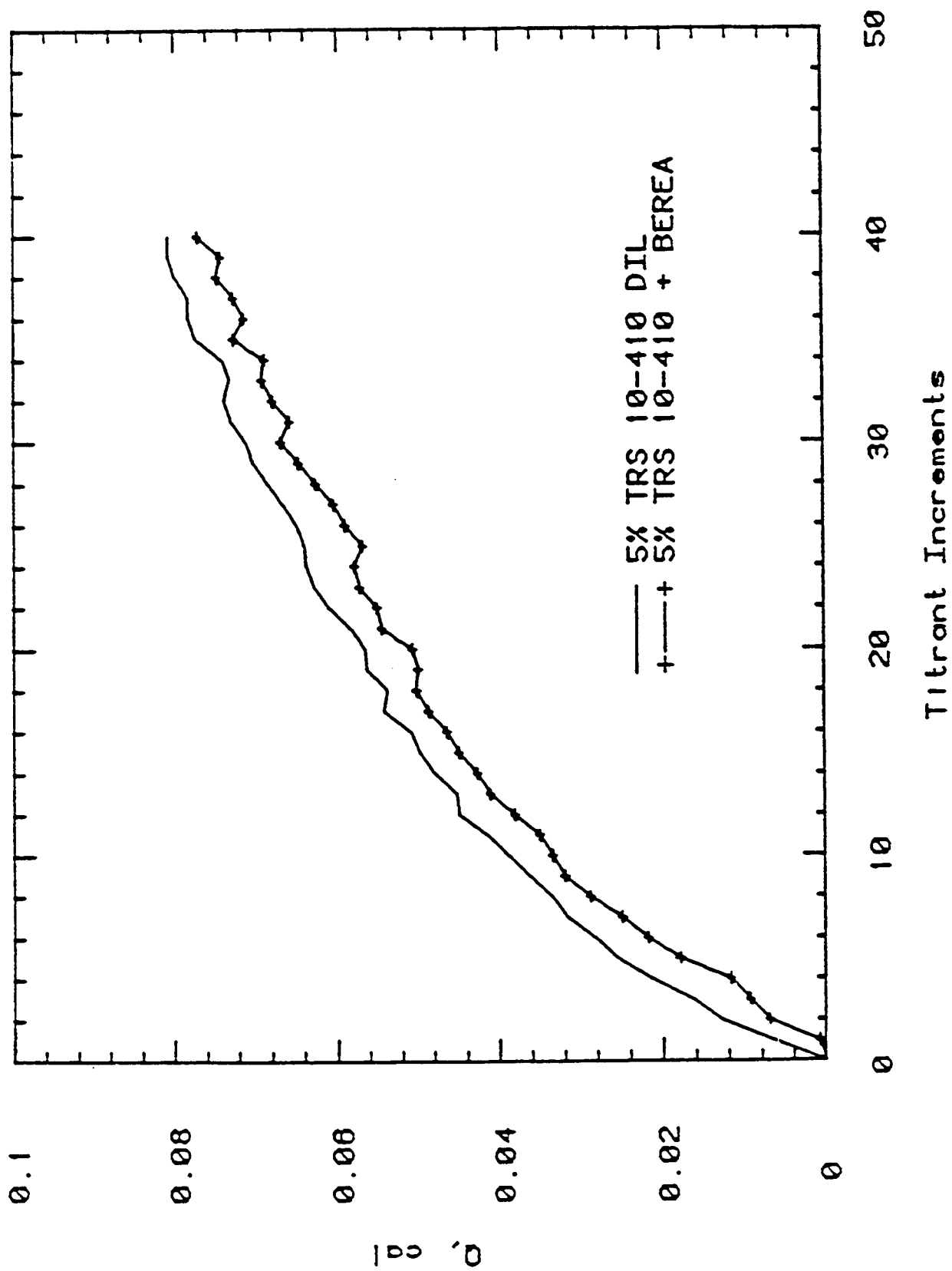
FIGURE 9. - Titration of powdered Berea sandstone by 5% TRS 10-410 compared with dilution of the surfactant.

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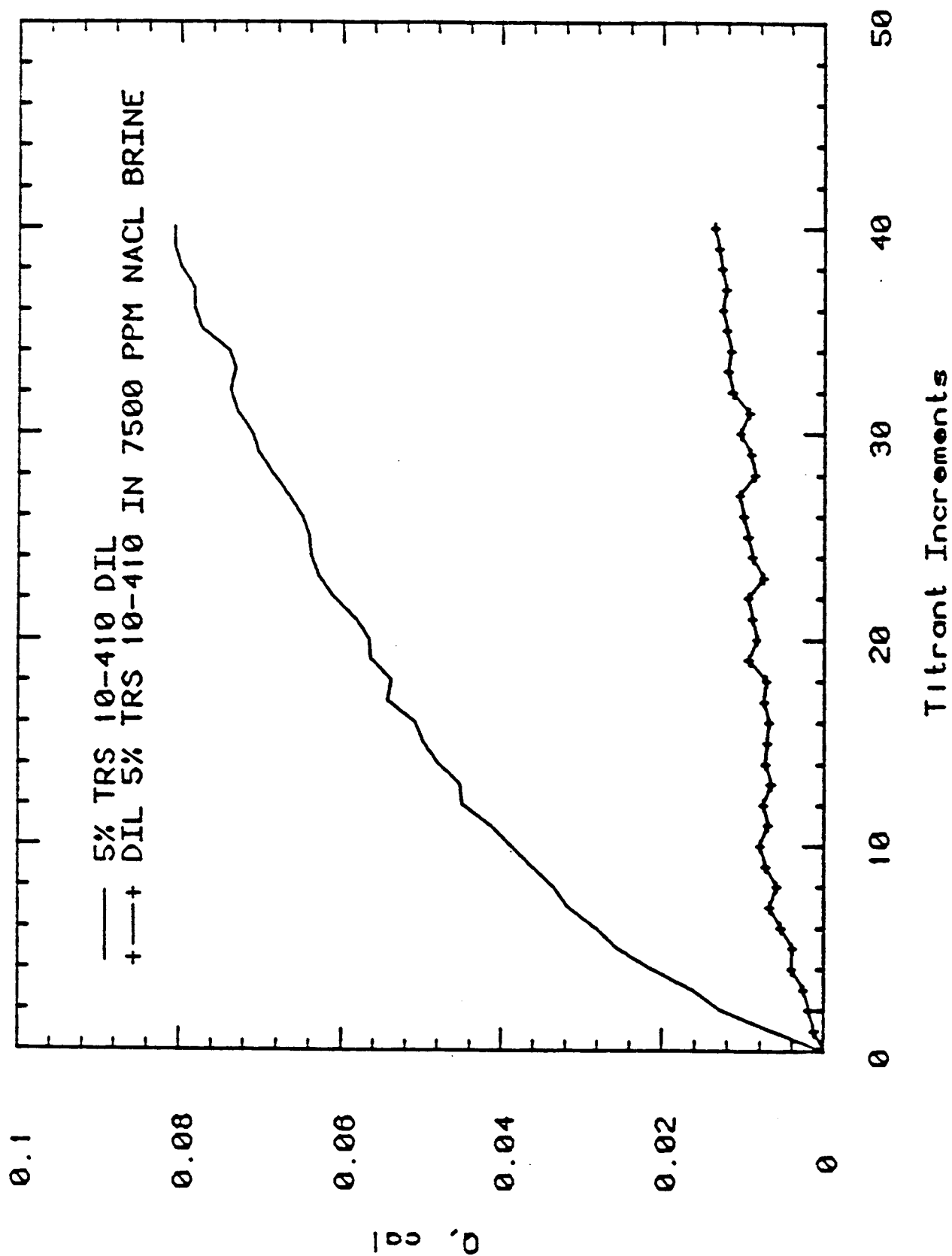
FIGURE 10. – Comparison of dilution of TRS 10-410 in fresh water and in brine.

TABLE 1. - Langmuir fitting parameters for 1-decanol adsorbed from heptane by silica

n_m	1.06 m mol/g
b	2070
H_m	-54.9 J/g
k	2326
H_m/n_m	-51.8 J/g
area per mole	0.56 nm^2

TABLE 2. - Specific area (m^2/g) and enthalpy of immersion of minerals (mJ/m^2)

	Area	H_2O	86,000 ppm NaCl	4% Aq n·BuOH
SiO_2	340	-147	-145	-149
Al_2O_3	181	-492		-472
Florisil	240	-209	-199	-193
$C_{18}SiO_2$	270	-13	-11	-9.9

TABLE 3. - Enthalpy of replacement and surface excess
from water, brine, and aqueous cosurfactant

Mole fraction	H_2O		86,000 ppm NaCl		4% Aq n-BuOH	
	$\Delta_{1,2}H$ mJ/m^2	adsorption μmol/m^2	$\Delta_{1,2}H$ mJ/m^2	adsorption μmol/m^2	$\Delta_{1,2}H$ mJ/m^2	adsorption μmol/m^2
SiO_2						
Triton X-100						
.00031	-10	2.0	-8.5	2.4	-9.1	1.8
.00063	-10	2.0	-8.5		-10.3	1.8
.00095	-10	2.0	-8.5		11.5	1.8
.0013	-10	2.0	-8.5		-12.3	1.8
Al_2O_3						
Triton X-100						
.00031	-.044	-.01				
.00063	-.044	.01				
.00095	-.044	-.01				
.0013	-.044	-.01				
SDDS						
.00065	-7.7	.82			-8.8	.67
.0013	-8.7	.94			-11.0	.83
.0020	-9.3	1.05			-12.7	.92
.0027	-9.8	1.16			-13.8	1.09

TABLE 3. – Enthalpy of replacement and surface excess from water, brine, and aqueous cosurfactant (cont'd.)

Mole fraction	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$
	H_2O		86,000 ppm NaCl		4% Aq n-BuOH	

Florisil

Mole fraction	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$
Triton X-100						
.00031	-9.6	.50	-17.1	.38	-12.1	.32
.00063	-9.6	.50	-17.1		-12.1	.31
.00095	-9.6	.50	-17.1		-12.1	.31
.0013	-9.6	.50	-17.1		-12.1	.32
SDDS						
.00065	-7.5	.75			-13.3	.077
.0013	-9.6	.75			-15.4	.14
.0020	-9.6	.83			-17.1	.21
.0027	-9.6	.83			-17.9	.27

$C_{18}SiO_2$

Mole fraction	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$	$\Delta_{1,2}H$ mJ/m^2	adsorption $\mu mol/m^2$
Triton X-100						
.00031	-31.7	1.98	-32.8	1.68	-30.2	1.64
.00063	-31.7	2.0	-32.8		-31.0	1.75
.00095	-31.7	2.0	-32.8		-31.7	1.94
.0013	-31.7	2.0	-32.8		-31.7	1.94
SDDS						
.00065	-21.1	1.38			-33.6	.98
.0013	-24.1	1.34			-39.2	1.28
.0020	-28.8	1.72			-42.2	1.64
.0027	-29.4	1.79			-44.4	1.99

TABLE 4. - Plateau molar enthalpies of adsorption (KJ/mole)
and molecular parking areas (nm^2/molecule)

	ΔH	H_2O area	86,000 ppm NaCl brine ΔH	area	4% Aq n-BuOH ΔH	area
Triton X-100						
SiO_2	-5.0	0.83	-3.54	0.69	-5.1	0.92
Florisil	-19.2	3.3	-45	4.4	-38	5.2
$C_{18}SiO_2$	-16	0.83	-19.5	1.0	-18.4	0.86
SDDS						
Al_2O_3	-9.4	1.43			-13.8	1.52
Florisil	-12.8	2.0			-66	6.2
$C_{18}SiO_2$	-18	0.93			-18.4	0.83

TABLE 5. – Dilution of stock surfactant solutions in the titration calorimeter

| Titrant | | ΔH |
Surfactant	Mass fraction	J
TR	.10	-0.404
TR	.20	-0.890
TR	.30	-1.882
TRS 10-410	.05	0.338
TRS 10-410	.05 in 7.5% NaCl	0.057
SDDS	.10	1.650

Table 6. – Interaction of solids with surfactant

| Solid | Titrant | | ΔH, | ΔH, J/g Flow |
	Surfactant	Mass fraction	J/g	Calorimeter
SiO_2	TR	.10	-2.09	
SiO_2	TR	.20	-2.83	
SiO_2	TR	.30	-3.04	-3.36
Charcoal	TR	.30	-15.9	-22
$C_{18}SiO_2$	TR	.10	-2.4	
$C_{18}SiO_2$	TR	.30	-7.6	-8.2
Berea	TR	.10	-0.081	
Berea	TRS 10-410	.05	-0.011	
Kaolin	TR	.10	-0.013	
Bentonite	TR	.10	-11.6	

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